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Microstructures and Superconductivity of Ultrathin $YBa_2Cu_3O_7$ Films

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We have studied conditions needed for the occurrence of superconductivity in one-unit-cell thick (1-UCT) $YBa_2Cu_3O_7$ (YBCO) grown on nonsuperconducting $PrBa_2Cu_3O_7$ (PrBCO). The cross-sectional transmission electron microscope observation reveals that the terminating atomic layer of YBCO is CuO layer. 1-UCT YBCO shows a superconducting transition when it is covered with BaO layer. This means that terminating CuO layer does not act as a hole donor until the charge reservoir layer of BaO-CuO-BaO is completely formed.

KEY WORDS: High-T_c superconductivity/ $YBa_2Cu_3O_7$/ Ultrathin film/ Terminating layer

INTRODUCTION

Recently, ultrathin films of high-T_c oxides have been extensively studied to address the two-dimensional (2D) nature in the superconductivity of the materials. We have revealed that high temperature superconductivity occurs in one-unit-cell (1-UCT) thick $YBa_2Cu_3O_7$ (YBCO) layer sandwiched between nonsuperconducting $PrBa_2Cu_3O_7$ (PrBCO) layers.[1) The superconducting transition of the 2D CuO_2 bilayer in the 1-UCT YBCO has been found to be well describable by Kosterlitz-Thouless model.[2)]

Understanding of microstructures of the ultrathin films on atomic scales is an essential issue for the discussion of the superconductivity in the ultrathin films. In our previous work,[3)] we have shown that YBCO is grown by 2D unit cell-by-unit cell growth manner from the observation of the reflection high energy electron diffraction (RHEED) intensity oscillations. We have pointed out that there should be a definite stacking sequence of atomic layers in the growth unit, and therefore, the terminating layer in the growth unit should always be the same. It is well recognized that hole donation into conducting CuO_2 planes from charge reservoir layers is of essential importance for the occurrence of superconductivity. As 1-UCT YBCO has only a set of two CuO_2 planes interposed with an Y layer, it would be a significant problem whether there is a charge reservoir layer on the CuO_2 bilayer or not.

In this paper, we report the microstructures of ultrathin YBCO films, especially the determination of the terminating layer of YBCO films in relation to the condition needed for the occurrence of superconductivity in 1-UCT YBCO.

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EXPERIMENTAL

Films were grown by reactive evaporation method,[4] i.e., coevaporation of metal elements under an oxygen atmosphere. A schematic diagram of the deposition system is shown in Fig. 1. Y, Pr and Ba metals were evaporated from electron-beam heated sources, and Cu metal was evaporated from thermal source. The evaporation ratio of the metals were controlled by oscillation quartz sensor located near the substrate. The oxygen gas was introduced to the substrate surface through an ozonizer system. The local gas pressure near the substrate was 10^{-2} Torr and the background pressure was kept at 10^{-4} Torr during the deposition. The low background pressure enabled us to use *in situ* RHEED observation during the growth of the films. The substrate was $SrTiO_3(100)$. The substrate temperature was 680°C and the deposition rate was 0.5Å/s. During the growth of YBCO, RHEED specular intensity shows definite oscillations caused by unit cell-by-unit cell growth and one period of the oscillations precisely corresponds to the height of one unit cell ($\approx$ 12Å). In this study, the ultrathin YBCO films were fabricated by interrupt growth technique through the monitoring of the RHEED specular intensity oscillations. The interruption time of 20s has been taken after every one unit cell growth in order to improve the surface flatness. After the deposition, films were cooled to room temperature in oxygen atmosphere.

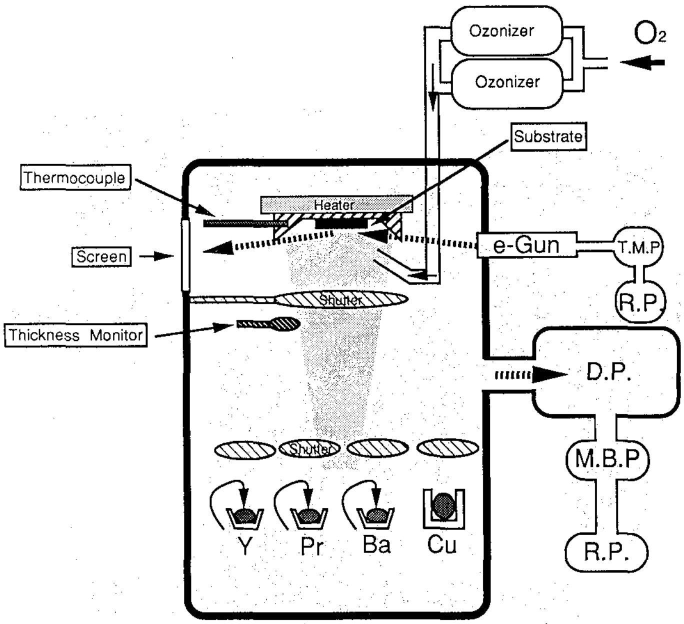


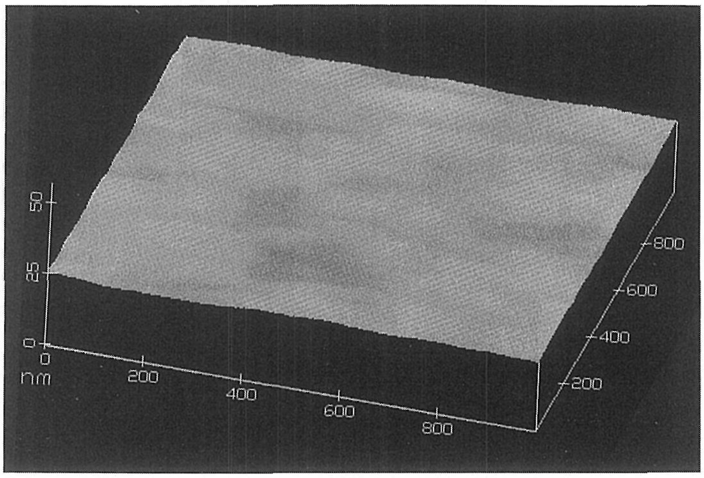
Fig. 1. Schematic diagram of the deposition system.

Surface morphology and microstructure of the films were investigated by atomic force microscopy (AFM) and transmission electron microscopy (TEM). Resistivity was measured by a conventional four-probe method.

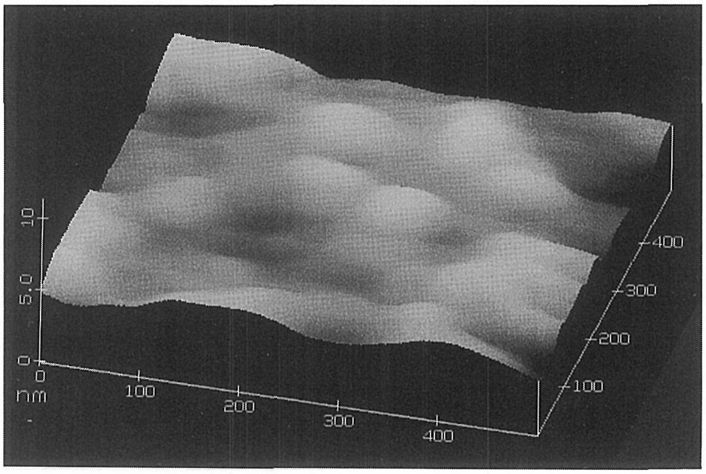
RESULTS AND DISCUSSION

Microstructure of ultrathin YBCO film

Low-magnification AFM image of a 12-UCT ($\approx$ 140Å) YBCO film is shown in Fig. 2 (a). The image reveals that there is no particulate and void which are often observed in the laser-ablated film. Although the area shown in the figure is restricted within 1 μm $\times$ 1 μm, we confirmed that the observation covering a wide area shows a similar image. Figure 2(b) shows a high-magnification image of the same film. The surface appears to be gentle up and down structure, implying 2D nuclei. Line scan across the film surface (Fig. 2 (c)) reveals that the vertical height of most nuclei is one-unit-cell length ($\approx$ 12Å) and the maximum roughness of the film is less than two-unit-cells length ($\approx$ 24Å).



(a)



(b)

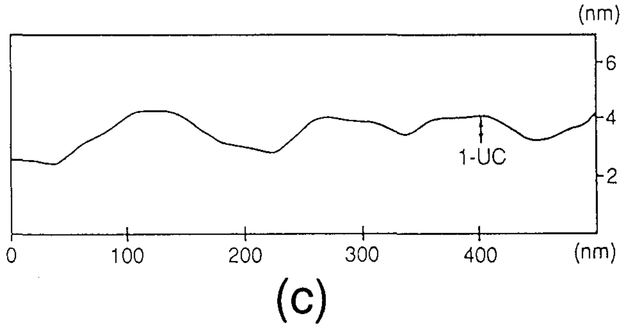


Fig. 2. (a) Low-magnification AFM image of a 12-UCT YBCO film. (b) Higher-magnification image of the film shown in (a). (c) Line scan profile along the surface of the film shown in (a). Height of one unit cell of YBCO is shown by a marker.

Recently, scanning tunneling microscope (STM) and atomic force microscope (AFM) observations have revealed that conventional spiral growth occurs in the sputtered[5,6] and laser-ablated[7] YBCO films. The microstructure of such films consists of spiral grains, each of which contains a screw dislocation at its center. Most of terraces around the screw dislocation are atomically flat and vertical height difference between the terraces is one or more unit cells. The film with spiral grains is, however, unfavorable for the study of the 2D nature of YBCO as well as the device application. We note that the high-magnification AFM profile and its line scan, exhibiting a repetition of up and down around a level, are strong evidence against the spiral growth.

The surface morphology revealing the 2D nuclei with the height of one unit cell and the appearance of the RHEED oscillations during the growth of the film definitely indicate that the growth manner of "ultrathin" YBCO on $SrTiO_3$ (100) by interrupt growth technique is 2D unit cell-by-unit cell. This type of growth implies that the growth unit has a definite terminating layer.

Figure 3 shows a cross-sectional TEM image at the surface of YBCO film. The surface of YBCO was covered *in situ* with Y_2O_3. Distinct contrast between YBCO and Y_2O_3 enables us to determine the terminating atomic layer of YBCO. The image simulation reveals that the terminating layer is CuO layer.

Superconductivity in 1-UCT YBCO

Figure 4 shows the resistance versus temperature curves for 1-UCT YBCO grown on 11-UCT PrBCO buffer layer with various cap layers. The 1-UCT YBCO without a cap layer shows nonsuperconducting behavior (curve *a*). When a La_2CuO_4 (001) layer is epitaxially grown, the film is also nonsuperconducting (curve *b*). This result of curve *b* indicates that surface degradation is not the origin of the nonsuperconducting behavior of film *a*. In contrast, the 1-UCT YBCO layer covered with 1-UCT PrBCO shows superconducting transition (curve *c*). The resistive transition curve of a bare 2-UCT YBCO layer (curve *d*) is similar to that of the 1-UCT YBCO layer covered with 1-UCT PrBCO (curve *c*). This similarity suggests that the surface 1-UCT layer of the bare 2-UCT YBCO layer does not

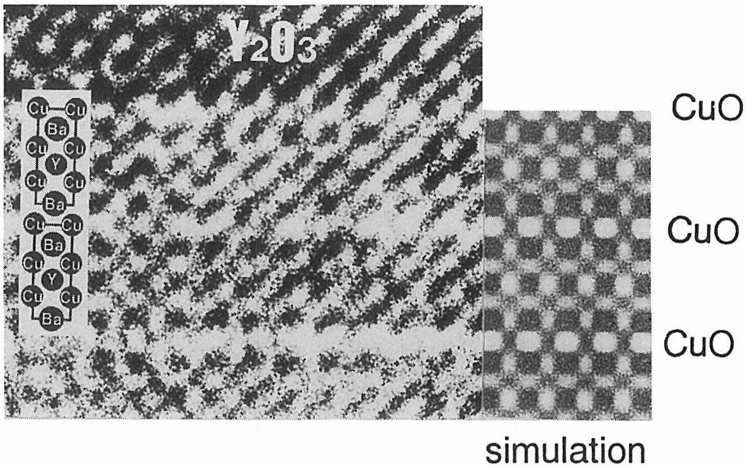


Fig. 3. Cross-sectional TEM image at the surface of YBCO.

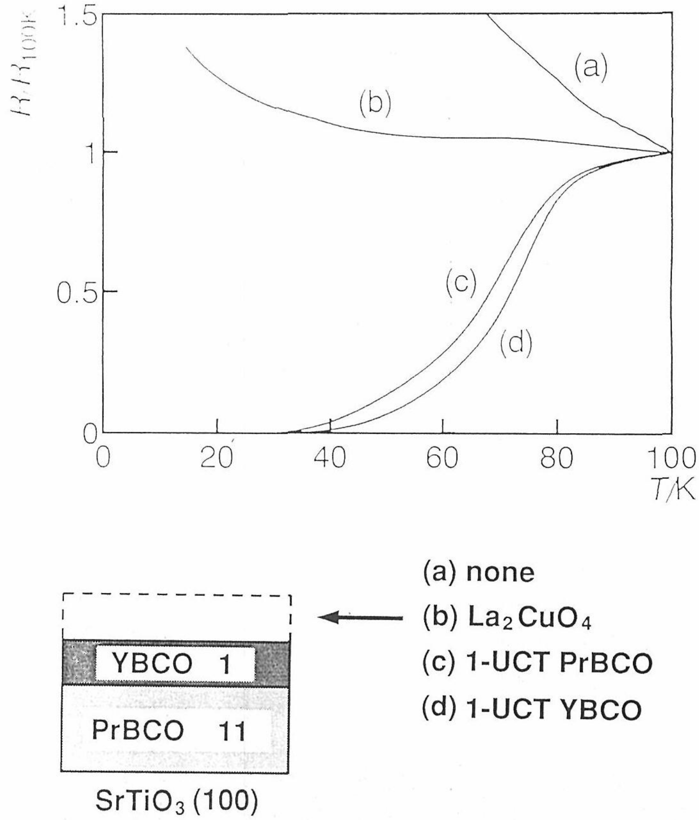


Fig. 4. Normalized resistance $[R(T)/R(100K)]$ vs temperature for X/YBCO(1-UCT)/PrBCO(11-UCT): X is, curve a, none; curve b, La_2CuO_4 (001); curve c, 1-UCT PrBCO; curve d, 1-UCT YBCO.

show superconductivity.

Figure 5 shows a stacking sequence of the atomic layers in 1-UCT YBCO grown on PrBCO layer. It is well recognized that the CuO chain layer plays a significant role in the hole donation into the conducting CuO_2 layers and the superconducting properties of YBCO are strongly affected by the short range ordering of oxygen atoms in the CuO chain layer.[8] When the YBCO is terminated by CuO layer, the surface CuO layer may not act as a hole donor because the oxygen atoms can not be ordered due to the lack of BaO layer. Absence of superconductivity in films *a, b* and the surface 1-UCT layer of the bare 2-UCT YBCO layer may be caused by a shortage of hole concentration due to an imperfect structure of the charge reservoir layer. The growth of PrBCO layer on 1-UCT YBCO layer guarantees the formation of BaO-CuO-BaO charge reservoir layer. If our model is correct, deposition of BaO layer on 1-UCT YBCO layer would give rise to a superconductivity in 1-UCT YBCO.

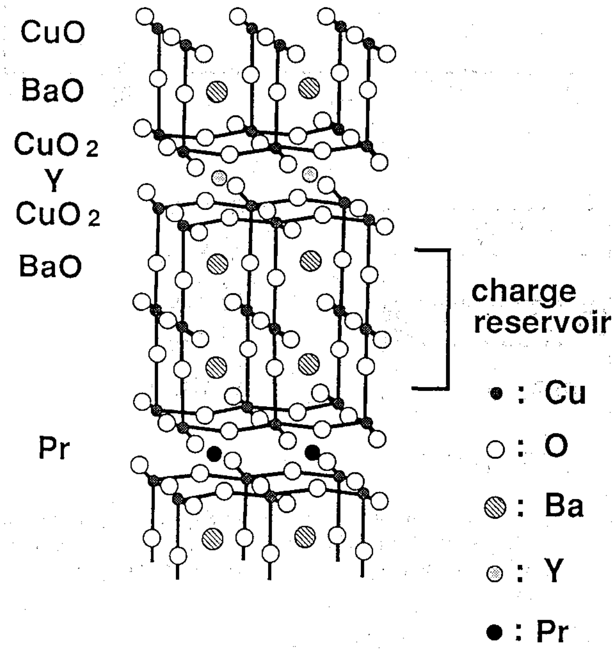


Fig. 5. Schematic illustration of the atomic layers in 1-UCT YBCO on PrBCO.

Figure 6 shows T-dependence of normalized resistance (R/R_{100K}) for samples of 1-UCT YBCO grown on 11-UCT PrBCO with cap layers, (a) none, (b) BaO, (c) SrO, (d) CaO, and (e) CuO. The thickness of each layer is fixed to be 8Å, which is thicker than one atomic layer of each oxide, in order to obtain an enough coverage. And, the surfaces of the capping layers were covered with PrO_x because the bare surfaces of BaO and SrO are unstable in air. Curve *b* clearly shows that capping by BaO makes 1-UCT YBCO superconducting. Furthermore, although the zero-resistance is not achieved by SrO capping, the film shows an obvious resistive onset of superconducting transition (curve *c*). This result indicates that the layer of SrO-CuO-BaO has also a capability of hole donation. On the other hand, capping with other layers proves to have no use in providing 1-UCT YBCO with hole carriers.

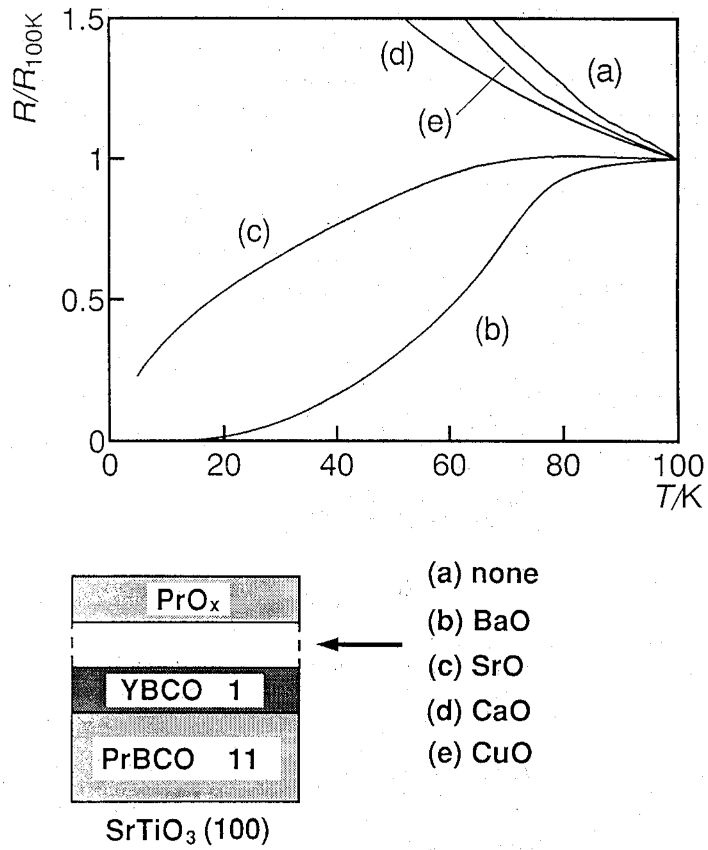


Fig. 6. Normalized resistance [$R(T)/R$(100K)] vs temperature for X/YBCO(1-UCT)/PrBCO(11-UCT): X is, curve a, none; curve b, BaO; curve c, SrO; curve d, CaO; and curve e, CuO.

CONCLUSION

The condition for the occurrence of the superconductivity in 1-UCT YBCO has been studied in relation to the microstructure of the film. TEM observation has revealed that the terminating layer of YBCO film grown on $SrTiO_3$ is CuO layer. The 1-UCT YBCO layer shows superconducting transition when BaO-CuO-BaO charge reservoir layers are located above and below the CuO_2 bilayer.

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